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Bezeichnung: Precious metal oxide catalyst for water electrolysis

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Precious metal oxide catalyst for water electrolysis

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Field of the Invention

The present invention is directed to catalysts for water
5 electrolysis, particularly to precious metal based
catalysts for PEM water electrolysis, regenerative fuel
cells (RFC) or oxygen generating electrodes in various
electrolysis applications. Furthermore, products containing
these catalyst materials, such as electrodes, catalyst-
coated membranes and membrane-electrode-assemblies are
10 disclosed.

Background of the invention

Hydrogen will become a major energy carrier in a future
15 energy regime based on renewable resources. Water
electrolysis is the most practical way to produce hydrogen
using renewable resources. Investment and production costs
of electrolysers define the total economy of the system and
will determine whether this is to become a feasible process
20 for hydrogen production. The production cost of hydrogen by
water electrolysis is, to a large extent, affected by the
electric power consumption, which can be about 70% of the
total production costs of hydrogen.

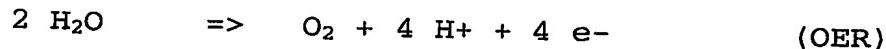
Two different types of water electrolysers are commonly
25 used in the state of the art: Alkaline electrolysers and
PEM water electrolysers. Water electrolysers using a
polymer electrolyte membrane ("PEM") along with precious
metal catalysts are able to operate at considerably higher
30 current densities and at lower specific energy consumption
compared to conventional alkaline electrolysers giving the
advantage of higher utilisation of the equipment and

reduced production costs. In the best PEM electrolyzers, a cell voltage of 1.67 V at 3 A/cm² has been obtained. This cell voltage is comparable to that of a modern alkaline electrolyser which typically is operating at 0.2 A/cm².

- 5 This means that the alkaline electrolyser needs 15 times larger active area to produce the same amount of hydrogen at the same electrical power consumption compared to a PEM electrolyser system. The present invention is therefore directed to improvements of catalysts for PEM electro-
- 10 lysers.

Generally, PEM water electrolyzers are built up similar to a PEM fuel cell, however, they are working in a different manner. During PEM fuel cell operation, oxygen reduction takes place at the cathode and hydrogen oxidation occurs at

- 15 the anode of the fuel cell. In summary, water and electrical current is produced. In a PEM water electrolyser, the current flow and the electrodes are reversed and water decomposition takes place. Oxygen evolution occurs at the anode (abbreviated "OER" = oxygen evolution reaction) and reduction of protons(H⁺), which travel through the polymer electrolyte membrane, takes place at the cathode (abbreviated "HER" = hydrogen evolution reaction). As a result, water is decomposed into hydrogen and oxygen by means of current. The reactions can
- 20 25 be summarized in the following equations:



- The PEM water electrolyser generally comprises a polymer electrolyte membrane (for example Nafion ® by DuPont), which is sandwiched between a pair of electrode layers and a pair of porous current collectors (or gas diffusion layers) mounted respectively on both sides of the electrode layers.

In PEM fuel cell electrodes, platinum on carbon catalysts are used for both, the anode electrocatalyst (for hydrogen oxidation) and the cathode electrocatalyst (for oxygen reduction). In the PEM electrolyser, carbon based materials such as Pt/carbon catalysts and carbon-fiber based gas diffusion layers (GDLs) cannot be used at the anode side because of corrosion of carbon by the oxygen evolved during water electrolysis.

For the manufacture of a membrane-electrode-assembly for a PEM electrolyser, catalyst inks comprising catalyst powder, solvents and optionally polymer electrolyte (i.e. "ionomer") material is prepared and applied either directly to the membrane or to the gas diffusion layer and then contacted with the membrane. The manufacture of this assembly is similar to the manufacture of membrane-electrode-assemblies (MEAs) for PEM fuel cells, which is broadly described in the literature (see for example US 5,861,222; US 6,309,772 and US 6,500,217).

Among all precious metals, platinum is the most active catalyst for the hydrogen evolution reaction (HER) at the cathode and can be applied at moderate loading. Iridium is well known for its unique electro-catalytic properties in respect to chlorine and oxygen evolution processes. Thus, iridium is the preferred material for the oxygen evolution reaction (OER) at the anode side, either in the form of pure metal or as oxide. However, for certain purposes, other precious metal oxides (i. e. oxides of ruthenium, platinum, rhodium, palladium, osmium and combinations thereof) can be employed.

In PEM water electrolysers, the precious metal catalyst loading on the anode and on the cathode is still relatively high, 3-5 mg p.m./cm² or more. Therefore there is a need for the development of improved catalysts with lower oxygen overvoltage and longer service life, which allows to reduce the catalyst loading of the electrolysers.

Description of related art

GB 1 195 871 describes the use of thermally treated RuO₂ and IrO₂ compounds and their mixtures in activated titanium electrodes (so-called „DSA”® = dimensionally stable anodes). The products are widely used for chlorine production in the chlor-alkali electrolysis. The ruthenium and iridium oxides are deposited by a thermal decomposition process of liquid precursors onto an electrically conductive titanium metal substrate. The addition of TiO₂ and various other inert oxides such as Ta₂O₅ or ZrO₂ is described to improve the longevity and stability of the electrode coating.

The deposition method by thermal treatment is not suitable for membrane-based PEM electrolyzers because of the low thermal stability of the polymer electrolyte membrane. Furthermore, the liquid precursors would penetrate the membrane and contaminate the ionomer material. Furthermore, the addition of TiO₂ and various other inorganic oxides occurs „in-situ”, i.e. before the formation of the precious metal oxide layer, a specific catalyst in powder form is not disclosed.

IrO₂/Pt electrocatalysts are reported by T. Ioroi et al [J. of Appl. Electrochemistry 31, 1179-1183 (2001) and J. of Electrochem. Soc. 147(6), 2018-2022 (2000)]. These catalysts were prepared in powder form by alkaline precipitation and subsequent thermal treatment. They do not contain any additional inorganic oxides.

US 2003/0057088 A1 is directed towards a PEM water electrolyser cell using an Ir-Ru anode catalyst comprising at least one metal selected from the group of iron (Fe), nickel (Ni) and cobalt (Co). These catalysts are to provide low oxidation overvoltages and are not eluted under the conditions of water electrolysis.

Various methods for manufacture of precious metal oxide powders are described in the literature. The most common method is the ADAMS-SHRINER method [ref.to R. Adams and R.L. Shriner, J. Am. Chem. Soc. 45, 2171 (1923)]: The
5 method consists of heating the chloride precursors (i.e. IrCl₃ or H₂IrCl₆) in an excess of sodium nitrate. This salt melt process creates a lot of toxic nitric oxide gases and must be performed in a batch process with low yields.

10 Summary of the invention

It was therefore the object of the present invention to provide improved precious metal oxide catalyst, which are suitable for use in PEM water electrolysis, reveal a low oxygen overvoltage, enable very low precious metal loadings
15 and can be manufactured in environmentally safe processes.

To achieve the above-cited objects, improved precious metal oxide catalysts as defined in the claims of the present invention were developed.

20 The claimed catalysts are basically composite catalyst materials and contain iridium oxide (IrO₂) and optionally ruthenium oxide (RuO₂) and/or other precious metal oxides in combination with a high surface area inorganic oxide (for example TiO₂, SiO₂, ZrO₂ and mixtures thereof). The term "composite catalyst" means that the materials contain
25 the precious metal oxide particles finely deposited on or dispersed around the inorganic oxide material.

The claimed materials are used as anode catalysts in PEM electrolyzers and reveal a very low oxygen overvoltage in water electrolysis (i.e. a low onset potential for oxygen evolution) and lead to a lower specific energy consumption per volume of hydrogen produced. Thus they offer higher hydrogen production rates at a given cell voltage. In summary, they can electrolyse water at a lower voltage than

conventional precious metal oxide based catalysts, which do not contain a high surface area inorganic oxide.

The catalyst-coated membranes ("CCMs") and membrane-electrode-assemblies ("MEAs") for PEM water electrolyzers
5 manufactured by use of the claimed precious metal oxide catalysts show improved performance vs. the state of the art materials.

As a consequence, smaller and cheaper electrolyser systems can be designed with less consumption of extensive
10 materials, such as ionomer membranes, precious metals and bipolar plates.

Detailed description of the invention

The present invention is directed to composite catalyst
15 materials comprising precious metal oxides, preferably iridium oxide (IrO_2) and optionally ruthenium oxide (RuO_2) and a high surface area inorganic oxide.

It was found that the presence of a high surface area inorganic oxide in the precious metal oxide catalyst
20 improves the catalyst performance in water electrolysis.

There is no detailed explanation for the phenomenon. In the course of the manufacturing process, the precious metal oxide particles are precipitated in very fine, nano-sized form (i.e. highly dispersed) on or at the surface of the inorganic oxide. If the BET surface area of the inorganic oxide is sufficiently high, the dispersion of the precious metal oxide particles remains stable during the subsequent thermal treatment process and sintering of the particles is prohibited. This results in a high BET surface area of the final catalyst, which in turn leads to high activity and stability. Optimum results were obtained when the BET surface area of the final precious metal oxide catalyst is
25
30

in the range of 40 to 100 m²/g. If the inorganic oxide is omitted, lower surface areas are obtained, resulting in a lower activity.

However, other explanations are feasible and may include
5 synergistic crystallinity effects, electrical conductivity phenomena and/or possible semiconductive properties of the inorganic oxide.

Suitable examples of inorganic oxides are pyrogenic ("fumed") oxides such as TiO₂, SiO₂ and Al₂O₃, manufactured
10 by Degussa AG, Duesseldorf. The preferred TiO₂ material is in the anatase modification and is manufactured by Sachtleben Chemie GmbH (Duisburg) under the product name "Hombifine N". Other examples are Nb₂O₅, SnO₂, doped tin oxide (SnO₂/F), ZrO₂, CeO₂/ZrO₂ and mixtures and combinations thereof. The inorganic oxides should be inert and
15 should have a very low solubility in water and acidic and caustic environments.

The inorganic oxide is added in a quantity of up to 20 wt.% based on the total weight of the precious metal oxide
20 catalyst. Preferably, the catalysts comprise about 90 wt.% precious metal oxide and about 10 wt.% inorganic oxide. To achieve best results, it was found that the BET surface area of the inorganic oxide should be in the range of 50 to 400 m²/g, preferably in the range of 100 to 300 m²/g.

25 In a typical preparation process, the high surface area inorganic oxide is thoroughly dispersed in an aqueous solution. Then the iridium precursor compound (Hexachloroiridium (IV) acid, Ir(III)-chloride, Ir-nitrate etc.) is added. The suspension is then heated to 70 - 100°C and
30 IrO₂ is subsequently precipitated by controlled addition of alkali to adjust the pH in a range of 6 to 10. After filtration and washing, the catalyst is dried and calcined at 300 to 500°C. The resulting catalyst is very active, has a high surface area, a very low degree of agglomeration and

can be easily dispersed in a catalyst ink for subsequent coating processes.

For the preparation of mixed Ir/Ru oxide catalysts, the above-cited process is modified and suitable Ir and Ru precursor compounds are jointly added to the suspension of the inorganic oxide in water. Suitable Ru-compounds are RuCl₃-Hydrate, Ru(III)-nitroyl-nitrate, Ru(III)-acetate and the like.

The heat treatment of the composite catalyst materials is performed in suitable batch or belt furnaces under air, reducing or inert atmospheres. Typical calcination temperatures are in the range of 300 to 800°C, preferably in the range of 300 to 500°C.

For manufacture of electrodes, catalyst-coated membranes (CCMs) and membrane-electrode-assemblies (MEAs), the precious metal oxide catalysts are processed into inks or pastes by use of suitable solvents and optionally ionomer materials. The catalyst inks are deposited onto gas diffusion layers (GDLs), current collectors, ionomer membranes, blank PTFE sheets, release papers or separator plates and the like by spraying, printing, doctor-blading or other deposition processes. Usually, a drying process is subsequently applied to remove the solvents of the catalyst ink. In catalyst-coated membranes and MEAs for PEM water electrolysers, the claimed catalyst materials are applied to the anode side of the MEA. The typical loading is in the range of 0,5 to 2,5 mg p.m./cm². On the cathode side, standard Pt catalysts (for example Pt/C or Pt-Black) are used. The cathode loadings are in the range of 0,2 to 1 mg Pt/cm².

The surface area measurements are conducted according to Brunauer, Emmett and Teller (BET) by the nitrogen adsorption method.

The electrochemical properties of the catalyst materials are determined by the measurement of the onset potential (in V) for oxygen evolution and the current density (in mA/cm²) at 1,5 V vs. NHE (in mA/mg). In these tests, the 5 catalyst samples are dispersed in a 5 wt-% alcoholic solution of Nafion® (Aldrich) and fixed on a glassy carbon electrode. Cyclic voltammograms are taken in sulfuric acid (c= 0,5 mol/l) at room temperature. Counter electrode is Pt, reference electrode is Hg/Hg₂SO₄ (Metrohm), scan speed 10 is 10 mV/s. The fifth scan of voltammograms is taken to generate quasi-stationary conditions.

The electrochemical activity is determined by two parameters (i) the onset of oxygen evolution and (ii) the current at a constant voltage of 1,5 V vs. NHE. The onset 15 of oxygen evolution is determined by linear extrapolation from a logarithmic plot of the potential (V vs. NHE, y-axis) vs. the current (mA/mg, x-axis).

The invention is illustrated but not limited by the following example and comparative example.

20

Example 1

Preparation of IrO₂/TiO₂(5 wt.%)

378,8 milligrams of titanium dioxide (Hombifine N, Sachtleben Chemie GmbH); BET > 300 m²/g) are added to a 1 25 liter beaker containing 112,5 ml of deionized water under vigorous stirring. Next, 29,7 grams of a hexachloroiridium acid solution (H₂IrCl₆, 24,3 wt.% Ir) are added to the suspension under stirring and diluted with 50 ml of deionized water. The suspension is then heated to 70°C. 30 After reaching the temperature, 50 ml of a 0,1 M NaOH-solution are added and diluted with further 500 ml of deionized water.

The final pH of 7,0 is adjusted using 10 wt.% NaOH. Temperature and pH are kept at the same level for about 4 hours. Finally the product is isolated by filtration and washed with 2 liters of deionized water. The catalyst is 5 dried in an vacuum oven overnight. The product is then calcined at 400°C in an box oven in air. The BET surface area remains very high at 66 m²/g, thus indicating the excellent catalytic activity of the material. Table 1 summarizes the characteristic data of the catalyst.

10

Comparative Example

Preparation of IrO₂ (without inorganic oxide)

150 ml of deionized water are poured into a 2 liter beaker. 15 24.86 grams of Hexachloroiridiumacid-hydratè (38,65 % wt. Ir) are dissolved in 50 ml of deionized water. The solution is added to the beaker under vigorous stirring and diluted with 50 ml of deionized water two times. The solution is heated to 70°C. After having reached the temperature, 4 grams of NaOH are dissolved in 50 ml of deionized water and 20 added to the solution under stirring.

The reaction solution is diluted with 500 ml of deionized water and a pH of 7,0 is adjusted by using 10 % wt. NaOH. Temperature and pH are kept at the same level for 4 hours. Finally the product is isolated by filtration and washed 25 with 1 l of deionized water. The catalyst is dried in an vacuum oven at 100°C overnight. The material is heat treated at 400°C. The BET surface area is lowered due to the absence of the inorganic oxide. Characteristic data are given in table 1.

30

Table 1:

Parameter	Example 1	Comparative Example
BET [m ² /g]	66	37
Onset-potential for the oxygen evolution [V]	1,47	1,65
Current density at 1,5 V vs. NHE [mA/mg]	1,48	0,23

5 When compared to example 1 (representing the invention), the comparative example shows a very high onset potential for oxygen evolution (1,65 V vs. 1,47 V of example 1).

This results in the fact that the current density at the given cell voltage of 1,5 V is very low (0,23 mA/mg vs.

10 1,48 mA/mg of example 1)

The data clearly demonstrate the superior characteristics of the catalysts of the present invention.

Claims

1. Precious metal oxide catalyst for water electrolysis comprising a composite of a precious metal oxide and an inorganic oxide.
- 5
2. Precious metal oxide catalyst according to claim 1, wherein the precious metal oxide is selected from the group of iridium, ruthenium, rhodium, osmium, platinum, palladium and/or combinations thereof.
- 10
3. Precious metal oxide catalysts according to claim 1, wherein the surface area of the composite catalyst is in the range of 40 to 100 m²/g.
4. Precious metal oxide catalysts according to claim 1, wherein the surface area of the inorganic oxide is in
- 15
5. Precious metal oxide catalyst according to claim 1, wherein the inorganic oxide is selected from the group of TiO₂, SiO₂, Al₂O₃, ZrO₂, SnO₂, CeO₂, Nb₂O₅, Ta₂O₅ and/or combinations thereof.
- 20
6. Precious metal oxide catalyst according to claim 5, wherein the inorganic oxide is added in a quantity of up to 20 wt.% based on the total weight of the catalyst.
7. Process for manufacture of a precious metal oxide catalyst according to claim 1 comprising the steps
- 25
- a) dissolving the precious metal precursor compound in the presence of the inorganic oxide in an aqueous solution and

- b) precipitating the precious metal oxide by adjusting the pH of the mixture in the range of 6 to 10.
- 8. Process according to claim 7, further comprising a
5 heat treatment of the catalyst at temperatures in the range of 300 to 800°C.
- 9. Electrode for PEM water electrolyzers, comprising the precious-metal oxide catalyst according to claim 1.
- 10. Catalyst-coated membrane for PEM water electrolyzers,
10 comprising the precious-metal oxide catalyst according to claim 1.
- 11. Membrane-electrode-assembly for PEM water electrolyzers, comprising the precious-metal oxide catalyst according to claim 1.
- 15 12. Use of the precious metal oxide catalyst according to claim 1 in fuel cells, sensors, electrolyzers and other electrochemical devices.

Abstract

- The invention is directed to precious metal oxide based catalysts for use as anode catalysts for PEM water electrolysis. The claimed composite catalyst materials comprise iridium oxide (IrO_2) and optionally ruthenium oxide (RuO_2) in combination with a high surface area inorganic oxide (for example TiO_2 , SiO_2 , ZrO_2 and mixtures thereof).
- 10 The claimed catalyst materials are characterised by a low oxygen overvoltage in water electrolysis. They enable a very low precious metal loading of electrodes, catalyst-coated membranes and membrane-electrode-assemblies for PEM electrolyzers.
- 15 The catalysts are used in fuel cells, sensors, electrolyzers and other electrochemical devices.

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